

Magnetic properties of polypyrrole - coated iron oxide nanoparticles

Raksha Sharma, Subhalakshmi Lamba and S. Annapoorni

Department of Physics and Astrophysics, University of Delhi, Delhi, India:110007

Abstract

Iron oxide nanoparticles were prepared by sol - gel process. In-situ polymerization of pyrrole monomer in the presence of oxygen in iron oxide - ethanol suspension resulted in a iron-oxide polypyrrole nanocomposite. The structure and magnetic properties of the nanocomposites with varying pyrrole concentrations are investigated. The X-Ray diffraction studies indicate the presence of $\gamma - Fe_2O_3$ phase for the concentrations investigated. FTIR studies confirm the presence of polypyrrole. The TEM studies show agglomeration in uncoated samples and in samples with a lower concentration of polypyrrole. Agglomeration is much reduced for samples coated with higher concentration of polypyrrole. The ac susceptibility measurements performed in the temperature range 77 - 300 K shows the presence of blocking, indicating the superparamagnetic phase. The blocking temperature is found to depend on the pyrrole concentration. Monte Carlo studies for an array of polydispersed single domain magnetic particles, based on an interacting random anisotropy model were also carried out and the blocking temperatures obtained from the simulation of the ZFC-FC magnetization compares favorably with experimental results.

Key words: nanocomposites, ac susceptibility, anisotropy, Monte Carlo

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1 Introduction

Over the recent years fine particle magnetic systems with particle sizes in the range of 5 to 50 nm have generated a lot of interest because of wide ranging technological applications like magnetic recording, electromagnetic shielding, sensors and magnetic refrigeration [1,2]. They exhibit a wide range of magnetic phases like ferromagnetism, antiferromagnetism, spin glasses etc. as well as the typical superparamagnetic behavior associated with single domain magnetic particles. The properties of these systems are sensitive to the particle size, interparticle interactions and temperature. The most commonly studied

magnetic nanomaterials are the oxides, in the form of ferrites and substituted ferrites. They are prepared by various processes like hydrothermal precipitation, sol - gel, sonochemical methods, sputtering, electron beam evaporation etc [3,4,5,6]. Among the standard methods, the sol - gel method has the advantage of good composition control and a low processing temperature. A critical obstacle in assembling and maintaining a nanoscale magnetic material is usually its tendency to agglomerate, which is a deterrent to its application for magnetic storage. This obstacle can be overcome if the particles are dispersed in a polymer matrix. Such nanocomposite materials are useful because of the processable nature of the polymers, a lesser tendency to agglomeration and a uniform particle size distribution in comparison to conventional nanomaterials.

Iron oxide polypyrrole nanocomposites can be prepared by several methods. In our laboratory these composites have been prepared by simultaneous gelation and polymerization[7]. The magnetic phase obtained was found to be very sensitive to the pyrrole concentration. We observed that these nanocomposites showed a change of phase to the non-magnetic $\alpha - Fe_2O_3$ phase for certain pyrrole concentrations. However since we wish to preserve the magnetic phase, we have now prepared the composites by allowing the polymerisation to occur with oxygen as the oxidizing agent, without using a soluble oxidant. Earlier workers have studied the properties of metal oxides like CuO , CeO_2 , NiO , SiO_2 and $\alpha - Fe_2O_3$ coated with PPy without soluble oxidants [8,9]. In the case of iron oxide particles it is expected that the polymer coating will result in well separated, smaller sized superparamagnetic particles which can be a good candidate for magnetic refrigeration and electromagnetic shielding [10].

Typically, transition metal oxide nanoparticles are characterized by a uniaxial anisotropy, and the relaxation between the two easy directions of magnetization leads to superparamagnetic behavior which is characterized by the blocking temperature. Theoretical research and modeling in nanomagnetic materials is somewhat restricted by the competing effects of disorder (in the shape, size and position of the particles), anisotropy and interactions, like the dipolar interactions and the exchange interactions. The systems have been investigated using mean field methods and thermodynamic perturbation theory [11,12,13]. In the light of the complexity of the system, numerical simulations become an effective tool for studying the system in detail. They can also provide valuable insight into the kind of material parameters that need to be synthesized for the purpose of application in devices. Here we present the results of Monte Carlo simulations based on a random anisotropy model for a single domain magnetic array, with anisotropy and interparticle interactions like long range dipolar and short range exchange. The simulations of the ZFC - FC magnetization are done for different values of the exchange parameter and the results appear to be in good agreement with the experimental results.

In Section 2 we discuss the experimental techniques, in Section 3 we discuss the results of the characterization and magnetic studies performed on the samples. In Section 4 we discuss the method and results of simulation and finally, in Section 5 we present our conclusions.

2 Experimental

Maghemite nanoparticles were prepared by the sol - gel method using ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) as precursor and 2 - methoxy ethanol as solvent [5,6,7]. The powder obtained by this method was suspended in distilled water and stirred using a magnetic stirrer for five hours. The above suspension was placed in a sonicator for 10 minutes. This resulted in a nonuniform suspension. This suspension was centrifuged at 5000 rpm for 20 minutes and further decanted. The remaining powder was heated to remove water and was used for coating with polymer.

1 gm of the dried powder was dispersed in a mixture of ethanol and deionized water in the ratio 7 : 10. About 0.2 ml of pyrrole monomer (Aldrich reagent grade, vacuum distilled, weight per ml of pyrrole is ~ 0.969 gm) was added to the above mixture. This was followed by the addition of 4 cc of 0.4% PVA solution. The PVA only acts as a binding agent and has no effect on the polymerisation [8]. A uniform mixture was obtained by placing the above mixture in an ultrasonic bath. This system was further diluted to 10 cc with deionised water. The whole mixture was then sealed tightly in a reaction vessel and heated at 85° C for 10 hours while being stirred continuously with a magnetic stirrer. The resulting solution was filtered and the powder obtained was washed thoroughly with distilled water. This method was followed for different pyrrole concentrations. Initial concentrations of iron oxide : pyrrole (monomer) were maintained in the ratios of 1 : 0.2, 1 : 0.8, 1 : 1.2 , 1 : 1.6 and 1 : 2.0.

The structural properties of the coated particles were investigated by XRD, using a Rigaku Rotaflex Diffractometer with a Cu - $K\alpha$ radiation ($\lambda = 1.54056$ Å). TEM was used to study the shape, size and morphology of the particle and was performed using a JEOL - JEM 2000 EX. The presence of polypyrrole was confirmed using FTIR, which was recorded using a Perkin Elmer FT-IR spectrometer, Spectrum 2000 model. A Rigaku PTC - 10 A thermobalance was used for investigating the degradation of the polymers. The magnetic measurements were performed in the temperature range 77 K to 300 K using a Lakeshore Cryotronics INC model 7000 AC Susceptometer. The measurements were performed at a field of 800 Amp/m and at a frequency of 16 Hz.

3 Results and Discussions

Our aim has been to obtain iron oxide polypyrrole nanocomposites with less agglomeration and retain the magnetic phase. In the above method it was observed that all the prepared samples were magnetic. The iron oxide powders obtained by the sol - gel process was light brown in color. With increasing concentration of pyrrole the color of the powders was found to change to dark brown and for concentrations higher than 1 : 1.6 they were found to be black, showing the presence of more polymer. As mentioned earlier PVA has been used only as a binder in our preparation and does not affect the polymerisation process. After confirming the degradation temperature of PVA by TGA - DTA measurements, all the samples were annealed at 250⁰ C to remove the excess PVA. The conductivity was measured and found to be very high (\sim M ohms), since no dopants were present in any of the composites.

The XRD studies performed on some of the nanocomposites is shown in Fig. 1. It is observed that all the annealed samples, annealed at 250⁰ C, retain the cubic $\gamma - Fe_2O_3$ phase. The lattice constant calculated from the diffraction pattern is $8.346 \pm .0001$ A and $c = 25.02 \pm .0001$ A and agrees well with reported values [18]. The grain size as estimated from the Scherrer's formula is ~ 20 nm.

In order to confirm the presence of polypyrrole the FTIR measurements were performed on the unannealed sample using KBr pellets. Fig 2 shows the FTIR for one of the nanocomposites namely 1 : 1.6. The peaks at 1096, 1620 and 3401 cm^{-1} are identified as the $C = C$, $N - H$ and $C - N$ bonds, respectively of the polymer backbone. The peaks appearing at 2343 and 2923 cm^{-1} belong to the $C - H$ and $-OH$ bonds of PVA. The peaks between 400 to 700 cm^{-1} corresponds to the $Fe - O$ bonds.

Fig 3(a) shows the TEM of the $\gamma - Fe_2O_3$ obtained from the sol - gel process which shows agglomerated iron oxide particles. Figure 3(b) shows the TEM for the smaller sized particles obtained after stirring, sonicating and centrifuging these particles. Although the grain size is reduced there is still agglomeration present. The TEM performed on one of the nanocomposite samples (1 : 1.6) is shown in Fig 3(c) which is seen to have much less agglomeration.

The TGA - DTA measurements were performed on several samples of varying concentrations of pyrrole in order to estimate the degradation temperatures of PVA and PPY. Fig 4(a) shows the DTA for one of the unannealed nanocomposites (1 : 1.6). It shows exothermic peaks at 210⁰, 300⁰ and 350⁰ C which corresponds to the degradation of PVA, degradation of pyrrole and phase change to $\alpha - Fe_2O_3$ respectively. The weight loss obtained from the TGA measurements indicates the amount of polymer present in the composites and

this is indicated in detail in Figure 4 (b). The weight is found to increase with increasing monomer concentration saturating beyond a concentration of 1 : 1.6 (Figure 4(b) inset).

Since we have carried out the oxidation of pyrrole only in the presence of air, it has been observed that even with an increasing monomer concentration the polymerization is very less. This is confirmed by the measurements above. The IR however shows the presence of PPy and hence it is likely that PPy grows around iron oxide core. This is markedly different from our observations on these composites when they were prepared by the simultaneous gelation - polymerization process which showed chain structure [7].

In Fig 5(a) and (b) we present the ac susceptibility results for two different concentrations namely 1 : 0.2 and 1 : 1.6 . For the low concentration sample the susceptibility increases with temperature till ~ 300 K. However for the higher concentration the χ' is found to increase and at ~ 180 K it starts decreasing, showing a clear transition to the superparamagnetic phase which is not evident in the sample with low concentration. The blocking temperature for the higher concentration as deduced from the susceptibility measurement is 180 K. The blocking temperature is not sharply defined, which is expected since we have a distribution in the particle sizes in the sample. In the low concentration samples there is a large amount of agglomeration, because of which the exchange interactions are present. This results in a higher blocking temperature [15,16]. Such behavior is also observed in rare earth clusters where even for very small particles (~ 2 nm) the blocking temperature observed is as high as 400 K [17]. The effect of coating of the $\gamma - Fe_2O_3$ particles with the polymer has resulted in smaller clusters with lesser interactions and hence lower blocking temperatures.

We have carried out Monte Carlo simulations on an interacting, random anisotropy model to study the effect of interactions on the blocking temperature of single domain magnetic particles.

4 Simulation

The model Hamiltonian for a system of interacting single domain magnetic particles, each having a magnetic moment vector $\vec{\mu}_i$ can be written as,[19],

$$H = -K \sum_i V_i \left(\frac{\vec{\mu}_i \cdot \vec{n}_i}{|\vec{\mu}_i|} \right)^2 - \sum_{\langle i \neq j \rangle} J_{ij} \vec{\mu}_i \cdot \vec{\mu}_j - \mu_0 \sum_{\langle i \neq j \rangle} \frac{3(\vec{\mu}_i \cdot \vec{e}_{ij})(\vec{\mu}_j \cdot \vec{e}_{ij}) - \vec{\mu}_i \cdot \vec{\mu}_j}{r_{ij}^3}$$

$$-\mu_0 \sum_i \vec{H} \cdot \vec{\mu}_i \quad (1)$$

The first term in Eq. 1 represents the anisotropy energy of the i th magnetic particle which has K as the anisotropy constant and V_i as its volume. Its magnetic moment vector is $\vec{\mu}_i$ and the direction of the easy axis of magnetization of the particle is represented by the unit vector \vec{n}_i . The second term is the exchange interaction energy between the different particles in the array and J_{ij} is the strength of the ferromagnetic exchange interaction between two particles with localized magnetic moment vectors $\vec{\mu}_i$ and $\vec{\mu}_j$ respectively. The third term is the dipolar interaction between these particles, with r_{ij} as the distance between the i th and j th particles and \vec{e}_{ij} the unit vector pointing along r_{ij} . The last term is the energy of the particles due to an externally applied magnetic field \vec{H} . For the purpose of simulation we assume that the magnetic moment vector for a single particle has a temperature independent magnitude and $\vec{\mu}_i = V_i M_S \vec{\sigma}_i$ where M_S is the saturation magnetization and $\vec{\sigma}_i$ is the unit vector along the direction of magnetization. We also assume that the exchange interaction has a site independent constant value $J_{eff} = J$. The method of preparation and the experimental observations indicate that magnetic nanoparticles in the sample are (i) not all of the same size and (ii) positioned randomly in the sample. Accordingly we work with a basic simulation cell which is a cube of size L^3 in which $N = 64$ single domain magnetic particles are randomly distributed. The volumes of the particles are picked from a normal distribution $P(V)dV = \frac{1}{(2\pi t^2)^{1/2}} \exp\left(-\frac{(V-V_0)^2}{2t^2}\right)$ where V_0 represents the mean volume of the particles which is taken to be equivalent to a sphere of diameter 15 nm and t is the width of the distribution which is taken to be .1. The directions of the easy axis of magnetization of the particles are also picked randomly. The dipolar interaction energy is calculated by summing over periodic repeats of the basic simulation cell by the method of Lekner summation [20,21].

The simulation of Field Cooled - Zero Field Cooled (FC-ZFC) magnetization is carried out by the Monte Carlo method using the standard Metropolis algorithm [17,22,23]. The value of $M_S = 4 \times 10^5$ Amp/m for $\gamma - Fe_2O_3$ is taken from literature. The magnetic field is kept fixed at .01 Tesla. To fit to the experimentally observed values of the blocking temperatures in these systems we find that the anisotropy constant should be higher than the reported values for the pure $\gamma - Fe_2O_3$ system which is $\sim .045 \times 10^5 J/m^3$. We find that appropriate results are obtained for a much higher value of the anisotropy constant, viz. $K = .1 \times 10^5 J/m^3$. This is keeping with the general trend seen that the values of the anisotropy constant observed for superparamagnetic iron oxide nanoparticles in a nanocomposite are usually quite high and for small particles of $\gamma - Fe_2O_3$ and Fe_3O_4 can be an order of magnitude larger than the values for bulk, in fact high as $2 - 4 \times 10^5 J/m^3$ [26,27]. The value of

J_{eff} is input as a parameter in the simulation. The purpose of the simulation is to estimate the blocking temperature from the FC- ZFC magnetization curves which are shown in Fig. 6, where we plot the variation of the scaled magnetization M/M_S with the temperature.

The relevant interactions in an assembly of single domain particles are the dipolar interactions and in this case, since there is clustering of the particles, exchange interactions. We find that the value of the blocking temperature is decided mainly by the anisotropy and the strength of the exchange interactions and not much by the dipolar interactions. The effect of dipolar interactions is more pronounced in the reduction of the magnetization. In curve (a) of Figure 6 we plot the FC - ZFC magnetization for a system in which the dipolar and exchange interactions are negligible (that is for a very dilute system of particles). We find that the blocking temperature T_B for this configuration is ~ 150 K. In curve(b) the dipolar interactions between the single domain particles are included in the simulation but the exchange interactions are neglected, the other parameters of the simulation remaining same as for curve(a). We find that (i) the magnitude of the magnetization is reduced and (ii) there is hardly any change in the value of T_B as compared to (a). In curves (c) and (d) we have plotted the FC - ZFC magnetization for the same simulation system for two different strengths of the exchange interaction J which are $J = .05E_A$ and $J = .1E_A$. E_A is the anisotropy energy of a spherical particle of radius $R_o = 7.5$ nm which is $K(4/3)\pi R_o^3$. The curves show some distinct features namely (i) the magnetization is enhanced compared to curve (b) which is expected because of the cooperative exchange interaction between the particles (ii) the blocking temperature is much higher, in range of 190 to 220 K (iii) the curves show a peaked structure and (iv) the FC curves show a double peak structure which is more pronounced in (d) and the same is reflected in the corresponding heating curve. The values of the T_B obtained from our simulation for (c) and (d) match well with experimental values (fig. 5). The enhancement of blocking temperatures and as well as the peak in the magnetization curves are known to be the effect of the interactions [1,11]. In particular, we feel that the double peaked structure below the blocking temperature which is seen only in the system with interactions and is more pronounced in the system with stronger interactions is a manifestation of competing interactions like dipolar and exchange in a system which further has strong disorder. It could also indicate some collective behaviour or memory-like effects, which however can be confirmed through further simulations which are now under progress. Similar behavior has also been observed experimentally recently [24,25]. We are in the process of conducting more detailed simulations to study the low temperature behaviour of these systems in more detail.

5 Conclusions

Polypyrrole coated iron oxide nanoparticles of varying monomer concentration were prepared and characterized using X-Ray, IR and TEM. The FTIR shows the presence of the polymer. The DTA - TGA analysis was used to determine the degradation temperature of polypyrrole which was found to be $\sim 300^{\circ}\text{C}$. Subsequently the samples were annealed at 250°C for further investigations. The X-Ray studies confirmed that the original $\gamma - \text{Fe}_2\text{O}_3$ phase was retained for all the composites prepared unlike in the case of simultaneous gelation - polymerization methods. TEM investigations clearly indicates smaller cluster sizes for higher concentrations of pyrrole. The ac susceptibility measurements performed on the uncoated and low pyrrole concentration sample did not show any blocking in the range of temperature 77 to 300 K. Samples with higher pyrrole concentration are superparamagnetic and show blocking at fairly high temperatures $\sim 180\text{ K}$. We feel that the higher blocking temperatures are a result of (i) larger anisotropy which is known in nanocomposites and (ii) cluster effects which lead to strong interparticle interactions. These results are supported by our simulation results which give blocking temperatures in the the range of 190 to 220 K depending on the strength of interaction. Hysteresis measurements are in progress to investigate the coercivity as a function of pyrrole concentration. By further refining the method of preparation of the composites as well as the matrix materials which are known to affect the anisotropy, we hope to obtain well separated smaller domains which would be of use in magnetic memory devices and refrigeration. Since the conducting polymers are organic semiconductors, dispersing magnetic nanoparticles in these would make them an interesting material for spintronic devices.

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Fig. 1. XRD patterns of (a) $\gamma - Fe_2O_3$ and polypyrrole coated $\gamma - Fe_2O_3$ of concentration (b) 1 : 0.8 (c) 1 : 1.6 and (d) 1 : 2.0 , all annealed at 250⁰ C.

Fig. 2. FTIR spectra of unannealed polypyrrole coated $\gamma - Fe_2O_3$ of concentration 1 : 1.6.

Fig. 3. (a) TEM of unannealed $\gamma - Fe_2O_3$ as obtained by sol -gel process (b) TEM of unannealed $\gamma - Fe_2O_3$ after magnetic breaking and (c)TEM of polypyrrole - $\gamma - Fe_2O_3$ nanocomposites of ratio 1 : 1.6.

Fig. 4. (a) DTA of unannealed polypyrrole - $\gamma - Fe_2O_3$ nanocomposite of ratio 1 : 1.2 (b)TGA of (1)pure iron oxide and $\gamma - Fe_2O_3$ -polypyrrole nanocomposites of following concentrations (2) 1.0:0.2 (3) 1.0:0.4 (4) 1:1.2 and (5) 1:2.0, inset shows the weight loss percentage with monomer volume in ml

Fig. 5. Variation of ac susceptibility with temperature for polypyrrole coated $\gamma - Fe_2O_3$ annealed at 250⁰ C of concentration (a) 1 : 0.2 and (b) 1 : 1.6.

Fig. 6. Variation of normalized magnetisation M/M_S with temperature T in K for a system with (a)no interactions(dipolar or exchange) (b)only dipolar interactions (c) dipolar interaction and exchange interaction of strength $J = .05E_A$ and (d) dipolar interaction and exchange interaction of strength $J = .1E_A$.

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